DATA EVALUATION RECORD

STUDY 3

CHEM 074801 S,S,S-Tributyl phosphorotrithioate §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41618816
Jackson, S.B., A. Kesterson, and L.J. Lawrence. 1988. Soil Surface Photolysis of [^{14}C]DEF in Natural Sunlight. Laboratory Project ID: Report No. 1153; Project No. 206. Mobay Report No. 95673. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Lexington, KY, and submitted by Mobay Corporation, Stilwell, KS.

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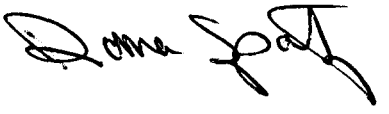
SIGNATURE: 

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is acceptable and fulfills the Photodegradation on Soil data requirement.

2. [^{14}C]S,S,S-Tributyl phosphorotrithioate was stable on sandy loam soil that was irradiated for 30 days with natural sunlight in Kentucky from February 4, 1988 thru March 5, 1988.

METHODOLOGY:

Monogahela sandy loam soil (48.02% sand, 49.65% silt, 2.33% clay, 1.45% organic matter, pH 6.6, CEC 10.33 meq/100 g) was air-dried, sieved (2 mm), and autoclaved. Portions of soil (3.1 g) were weighed into Petri dishes and 3.0 mL of distilled water were added to each dish. The slurries were air-dried, leaving a soil thickness of approximately 0.5 mm. [^{14}C]S,S,S-Tributyl phosphorotrithioate (DEF; radiochemical purity 98.9%, specific activity 20.4 mCi/mMol, Mobay), dissolved in acetonitrile, was applied evenly to the soil surface at 9.2 ppm with a syringe. The Petri dishes were placed in two steel chambers; one chamber was covered with a quartz plate and the other chamber was covered with a glass plate covered with black neoprene rubber to serve as a dark control (Figure 2). Both chambers were adjusted to a 30 degree angle with respect to the horizontal and were irradiated outdoors with natural sunlight from February 4 to March 5, 1988 in Lexington, Kentucky (38.05° N, 84.30° W). Sunlight intensity was continuously measured with a photodetector equipped with a quartz-enclosed probe; the photodetector was located on the roof near the exposure apparatus and was also tilted at a 30 degree angle. The temperature of the samples was maintained by circulating an antifreeze:water (1:1) solution through a water jacket using a constant temperature circulator; the temperature was monitored throughout the study using thermocouples attached to the soil surface with epoxy resin, and ranged from -9.3 to 41.5°C. Ambient air was drawn through the chambers using a vacuum pump and into glass dispersion tubes containing ethylene glycol to trap volatile compounds. Duplicate irradiated and dark control dishes were removed for analysis at 0, 5, 10, 15, 20, and 30 days posttreatment. Upon removal, the dishes were covered with parafilm and aluminum foil and placed in the refrigerator until extraction (the same day). The ethylene glycol traps were replaced at each sampling interval.

The soil was scraped from the petri dish into a flask; the dishes were rinsed twice with acetonitrile, and the rinses were added to the flask. Additional acetonitrile was added to the flask and the slurry was stirred for 1 hour. The slurry was vacuum-filtered, the flask was rinsed with additional acetonitrile, and the rinses were combined with the extract. Aliquots of the extract were analyzed by LSC. Additional aliquots of the extract were removed and refrigerated in the dark until analysis by HPLC. The extracted soils from the irradiated 30-day samples were dried and reextracted with methanol. Aliquots of the methanol extract were analyzed by LSC; additional aliquots were refrigerated until analysis by HPLC.

Prior to HPLC analysis, the soil extracts were fortified with unlabeled reference standards of S,S,S-tributyl phosphorotrithioate, butyl mercaptan, and dibutyl disulfide (purities not reported). Aliquots of the fortified extracts were analyzed by HPLC on a Zorbax TMS column eluted with an isocratic mobile phase of 85% acetonitrile: water:acetic acid (45:55:0.4):15% acetonitrile with UV (254 nm) detection. Radioactivity was identified with a radioactivity flow

detector or column fractions were collected and analyzed by LSC. The detection limit was 0.6 μg S,S,S-tributyl phosphorotrithioate/ fraction. Additional aliquots of extracts from the irradiated soil from the 15- and 30-day posttreatment sampling intervals (one replicate each) were analyzed by TLC on silica gel plates developed in acetonitrile:water:acetic acid (55:45:0.4). Unlabeled standards were cochromatographed with the samples and were visualized under UV light. The plates were marked and scraped in one centimeter bands into scintillation vials. Scintillation cocktail was added and the vials were counted by LSC. The extracted soil was air-dried and subsamples were analyzed by LSC following combustion. Triplicate aliquots of the ethylene glycol traps were analyzed by LSC.

DATA SUMMARY:

[^{14}C]S,S,S-Tributyl phosphorotrithioate (DEF; radiochemical purity, 98.9%), at 9.2 ppm, was stable on a sandy loam soil irradiated for 30 days with natural sunlight in Kentucky during February and March, 1988. The daily light energy was an average of 19 ± 1.5 W-min/cm^2.

The parent compound, S,S,S-tributyl phosphorotrithioate, was 100% of the acetonitrile-extracted radioactivity at 30 days posttreatment in both the irradiated and control samples (Table 6). At 30 days posttreatment, the acetonitrile-extractable radioactivity was 66.0-71.9% of the applied radioactivity in the irradiated samples and 85.4-86.6% in the dark controls (Table 5). After acetonitrile extraction, the total radiocarbon present in extracted soil ranged from 1.2% to 22.2%; (1.2-10.0% of the applied in the dark controls). Subsequent methanol extraction of Day 30 irradiated replicates removed 10.8% and 11.2% of the unextracted residues, leaving 9.5% and 9.3% remaining bound.

In the methanol extracts from the 30-day posttreatment samples, the degradate

butyl mercaptan

was 96.3-100% of the methanol-extracted radioactivity.

Residues remaining in the acetonitrile-extracted soil were 1.2-6.6% of the applied radioactivity immediately posttreatment; at 20-30 days posttreatment, these residues were 20.3-22.2% in the irradiated samples and 7.3-9.2% in dark controls (Table 5).

Volatile radioactivity in the ethylene glycol traps was ≤1.0% of the applied radioactivity,

The material balances were 84.3-104.5% (Table 5).

COMMENTS:

1. The study authors stated that S,S,S-tributyl phosphorotrithioate is stable to photolysis, yet the presence of butyl mercaptan in the methanol extract indicates that some degradation occurred. However, based on the results of the extraction of the 30-day sample, the estimation of a half-life from these data would be of limited value since the calculations would involve considerable extrapolation.

2. An unidentified degradate, present at 3.4% of the recovered radioactivity, was detected in one replicate of the dark control soils from the 15-day sampling interval. The study authors stated that it was most likely an artifact because it did not appear in subsequent samples.

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Table 1. Physical Characteristics of Soil Used in This Study.

Parameter	
pH	6.6
Texture Class: (Sandy Loam)	
Sand	48.02 %
Silt	49.65 %
Clay	2.33 %
Organic Matter	1.45 %
Cation Exchange Capacity	10.33 meq/100g

Table 2. Schedule of Events Throughout Study Period.

Study Day	Date	Time [1] Sunrise [2]	Time [1] Sunset [2]	Samples Taken	Time Taken
0	02-04-88	7:41	18:05	Day - 0	17:30
1	02-05-88	7:40	18:06		
2	02-06-88	7:39	18:07		
3	02-07-88	7:38	18:08		
4	02-08-88	7:37	18:09		
5	02-09-88	7:36	18:10	Day - 5	15:30
6	02-10-88	7:35	18:11		
7	02-11-88	7:33	18:11		
8	02-12-88	7:32	18:14		
9	02-13-88	7:31	18:15		
10	02-14-88	7:30	18:16	Day - 10	15:00
11	02-15-88	7:29	18:17		
12	02-16-88	7:28	18:18		
13	02-17-88	7:26	18:19		
14	02-18-88	7:25	18:20		

1 Eastern Standard Time.

2 Information received from the National Weather Service, Lexington, Kentucky.

Table 2 (Continued). Schedule of Events Throughout Study Period.

Study Day	Date	Time [1] Sunrise [2]	Time [1] Sunset [2]	Samples Taken / Time Taken	
15	02-19-88	7:24	18:21	Day - 15	15:00
16	02-20-88	7:23	18:22		
17	02-21-88	7:21	18:23		
18	02-22-88	7:20	18:24		
19	02-23-88	7:19	18:25		
20	02-24-88	7:18	18:26	Day - 20	14:30
21	02-25-88	7:16	18:27		
22	02-26-88	7:15	18:29		
23	02-27-88	7:13	18:30		
24	02-28-88	7:12	18:31		
25	02-29-88	7:12	18:32		
26	03-01-88	7:11	18:32		
27	03-02-88	7:09	18:33		
28	03-03-88	7:08	18:34		
29	03-04-88	7:06	18:35		
30	03-05-88	7:05	18:36	Day - 30	19:00

1 Eastern Standard Time.

2 Information received from the National Weather Service, Lexington, Kentucky.

Table 4. Light Intensity and Energy Measurements Throughout Study Period.

Study Day	Date	Light Intensity ($\mu W/cm^2$)			Total Light Energy ($W \cdot min/cm^2$)	
		Minimum	Maximum	Mean ± S.D.	per Day	Cummulative
0	02-04-88	59	47714	24842 ± 11088	17	
1	02-05-88	171	57075	25282 ± 10226	18	35
2	02-06-88	189	61388	25530 ± 10654	18	53
3	02-07-88	1014	59666	25716 ± 10695	17	70
4	02-08-88	177	32918	26603 ± 12217	19	89
5	02-09-88	56	71070	26869 ± 12912	19	108
6	02-10-88	90	54335	24761 ± 10683	17	125
7	02-11-88	34	74716	27603 ± 14273	19	144
8	02-12-88	71	52847	25344 ± 9955	18	162
9	02-13-88	129	46724	25129 ± 8719	18	180
10	02-14-88	45	67023	25889 ± 11849	18	198
11	02-15-88	62	85990	32540 ± 22106	24	222
12	02-16-88	306	59387	26197 ± 9526	18	240

Table 4 (Continued). Light Intensity and Energy Measurements Throughout Study Period.

Study Day	Date	Light Intensity ($\mu W/cm^2$)			Total Light Energy ($W \cdot min/cm^2$)	
		Minimum	Maximum	Mean ± S.D.	per Day	Cummulative
13	02-17-88	177	50706	25786 ± 8956	19	259
14	02-18-88	30	59100	27315 ± 12241	18	277
15	02-19-88	34	73762	28338 ± 18930	21	298
16	02-20-88	52	43773	26211 ± 9444	19	317
17	02-21-88	50	60387	25297 ± 9831	19	336
18	02-22-88	51	56703	25407 ± 9276	19	355
19	02-23-88	50	52119	24784 ± 10359	18	373
20	02-24-88	23	59928	25340 ± 10387	19	392
21	02-25-88	54	42825	25093 ± 8802	19	411
22	02-26-88	39	36679	25166 ± 8603	19	430
23	02-27-88	54	59361	26334 ± 9667	20	450
24	02-28-88	60	49194	25261 ± 8889	19	469
25	02-29-88	60	45780	25336 ± 8633	19	488

Table 4 (Continued). Light Intensity and Energy Measurements Throughout Study Period.

Study Day	Date	Light Intensity ($\mu W/cm^2$) Minimum	Maximum	Mean ± S.D.	Total Light Energy ($W \cdot min/cm^2$) per Day	Cummulative
26	03-01-88	58	58709	25446 ± 9532	19	507
27	03-02-88	401	79526	31288 ± 17856	23	530
28	03-03-88	134	61682	26315 ± 12091	20	550
29	03-04-88	313	47835	23357 ± 11668	17	567
30	03-05-88	34	74709	25972 ± 11318	19	586
Mean ± S.E.				26140.4 ± 320.6		
Mean ± S.D.		131.5 ± 185.4	76891.3 ± 107397.5		19 ± 1.5	

Table 5. Material Balance of [^{14}C]DEF Throughout the Study Period.

Sample Description	DPM Applied	DPM Recovered						Percent Total Recovery
		Extract	(%)	Extracted Solids	(%)	Gas Dispersion Trap	(%)	
Day - 0								
Dark Control 1	4,056,280	3,853,500	(95.0)	265,976	(6.6)	---		101.6
Dark Control 2	4,056,280	3,786,795	(93.4)	48,393	(1.2)	---		94.6
Irradiated 1	4,056,280	3,954,769	(97.5)	87,453	(2.2)	---		99.7
Irradiated 2	4,056,280	3,839,198	(94.6)	67,070	(1.7)	---		96.3
Day - 5								
Dark Control 1	4,056,280	3,833,596	(94.5)	400,713	(9.9)	5,580	(0.1)	104.5
Dark Control 2	4,056,280	3,619,404	(89.2)	368,849	(9.1)	5,580	(0.1)	98.4
Irradiated 1	4,056,280	3,482,550	(85.9)	382,573	(9.4)	13,255	(0.3)	95.6
Irradiated 2	4,056,280	3,505,140	(86.4)	547,284	(13.5)	13,255	(0.3)	100.2
Day - 10								
Dark Control 1	4,056,280	3,406,519	(84.0)	339,136	(8.3)	6,598	(0.2)	92.5
Dark Control 2	4,056,280	3,309,741	(81.6)	404,298	(10.0)	6,598	(0.2)	91.8
Irradiated 1	4,056,280	2,981,295	(73.5)	720,940	(17.8)	19,745	(0.5)	91.8
Irradiated 2	4,056,280	2,896,452	(71.4)	502,632	(12.4)	19,745	(0.5)	84.3

Table 5 (Continued). Material Balance of [^{14}C]DEF Throughout the Study Period.

Sample Description	DPM Applied	DPM Recovered: Extract	(%)	Extracted Solids	(%)	Gas Dispersion Trap	(%)	Percent Total Recovery
Day - 15								
Dark Control 1	4,056,280	3,879,134	(95.6)	157,176	(3.9)	13,119	(0.3)	99.8
Dark Control 2	4,056,280	3,655,170	(90.1)	227,700	(5.6)	13,119	(0.3)	96.0
Irradiated 1	4,056,280	3,445,676	(85.0)	543,328	(13.4)	31,303	(0.8)	99.2
Irradiated 2	4,056,280	3,347,388	(82.5)	536,284	(13.2)	31,303	(0.8)	96.5
Day - 20								
Dark Control 1	4,056,280	3,695,475	(91.1)	295,900	(7.3)	16,303	(0.4)	98.8
Dark Control 2	4,056,280	3,659,590	(90.2)	341,222	(8.4)	16,303	(0.4)	99.0
Irradiated 1	4,056,280	2,774,706	(68.4)	880,595	(21.7)	31,303	(0.8)	90.9
Irradiated 2	4,056,280	2,925,504	(72.1)	899,819	(22.2)	31,303	(0.8)	95.1
Day - 30								
Dark Control 1	4,056,280	3,466,075	(85.4)	372,818	(9.2)	40,833	(1.0)	95.6
Dark Control 2	4,056,280	3,512,600	(86.6)	340,999	(8.4)	40,833	(1.0)	96.0
Irradiated 1	4,056,280	2,677,485	(66.0)	821,450	(20.3)	35,980	(0.9)	87.2
Irradiated 2	4,056,280	2,916,144	(71.9)	832,129	(20.5)	35,980	(0.9)	93.3
						Mean + S.D. =		95.8 ± 4.57

Table 6. Quantitative Characterization of [^{14}C]DEF and Its Degradates Extracted From Soil Surfaces Following Exposure to Natural Sunlight.

Sample Description	HPLC Volume Injection (µl)	Percent of Total Extracted Radiocarbon As: DEF	Unknown
Day 0			
Irradiated 1	25	100.0	
Irradiated 2	25	100.0	
Mean		100.0	
Dark Control 1	25	100.0	
Dark Control 2	25	100.0	
Mean		100.0	
Day 5			
Irradiated 1	25	100.0	
Irradiated 2	25	100.0	
Mean		100.0	
Dark Control 1	25	100.0	
Dark Control 2	25	100.0	
Mean		100.0	
Day 10			
Irradiated 1	100	100.0	
Irradiated 2	100	100.0	
Mean		100.0	
Dark Control 1	100	100.0	
Dark Control 2	100	100.0	
Mean		100.0	

Table 6 (Continued). Quantitative Characterization of [^{14}C]DEF and Its Degradates Extracted From Soil Surfaces Following Exposure to Natural Sunlight.

Sample Description	HPLC Volume Injection (µl)	Percent of Total Extracted Radiocarbon As: DEF	Unknown
Day 15			
Irradiated 1	100	100.0	
Irradiated 2	50	100.0	
Mean		100.0	
Dark Control 1	100	97.1	2.9
Dark Control 2	100	96.1	3.9
Mean		96.6	3.4
Day 20			
Irradiated 1	100	100.0	
Irradiated 2	100	100.0	
Mean		100.0	
Dark Control 1	100	100.0	
Dark Control 2	50	100.0	
Mean		100.0	
Day 30			
Irradiated 1	50	100.0	
Irradiated 2	20	100.0	
Mean		100.0	
Dark Control 1	100	100.0	
Dark Control 2	50	100.0	
Mean		100.0	

$(CH_3CH_2CH_2CH_2S)_3P=O$

DEF

PTRL NO. 203-4

$CH_3CH_2CH_2CH_2S=SCH_2CH_2CH_2CH_3$

Dibutyl Disulfide

PTRL NO. 202-2

$CH_3CH_2CH_2CH_2SH$

Butyl Mercaptan

PTRL NO. 203-3

Figure 1. Chemical Structures of [^{14}C]DEF and Its Degradation Products.

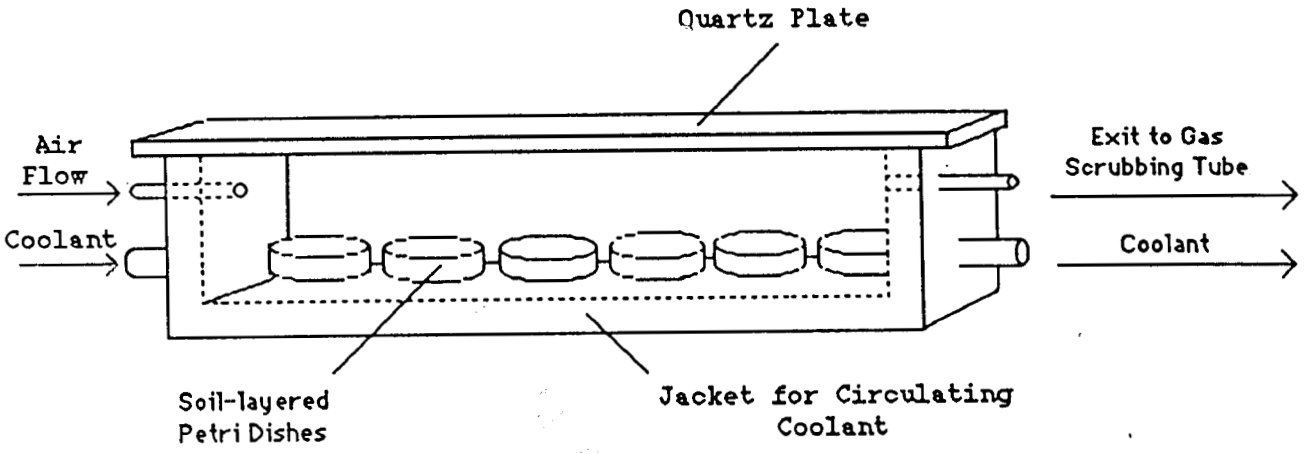

Figure 2. Apparatus Used to Expose [^{14}C]DEF on a Soil Surface to Natural Sunlight.

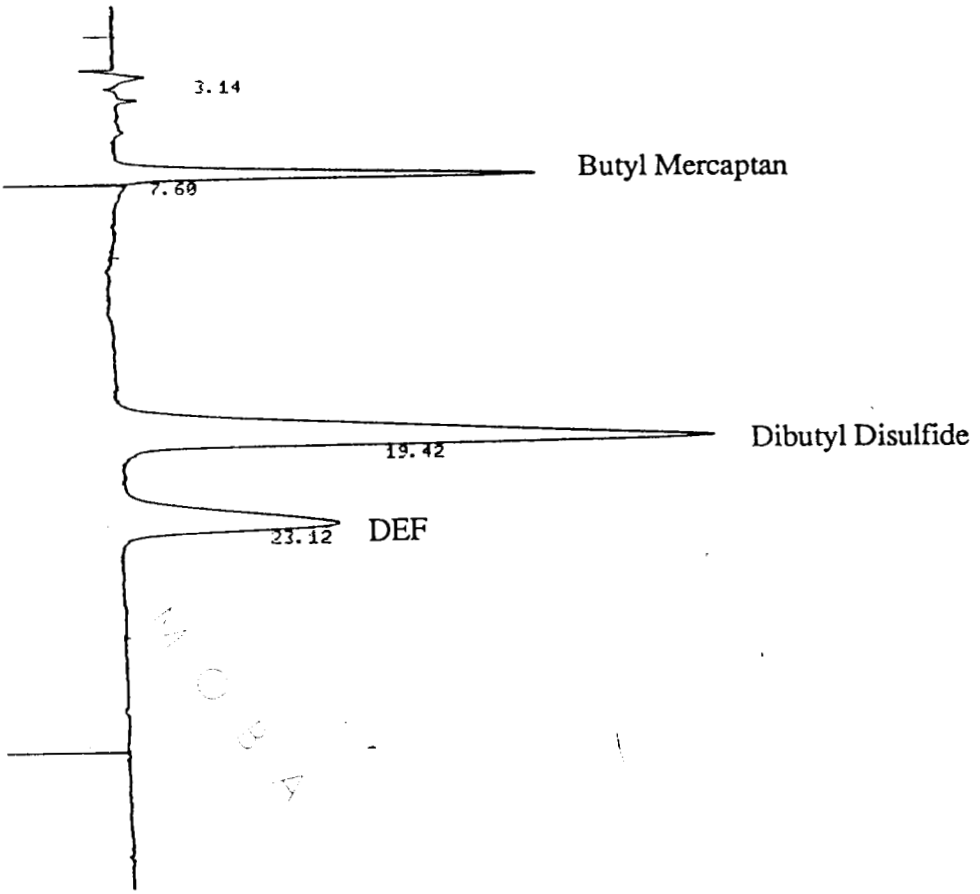

Figure 3. Representative Chromatogram of Analytical Standards of DEF and Its Degradation Products.

Day 30 Irradiated Replicate 1

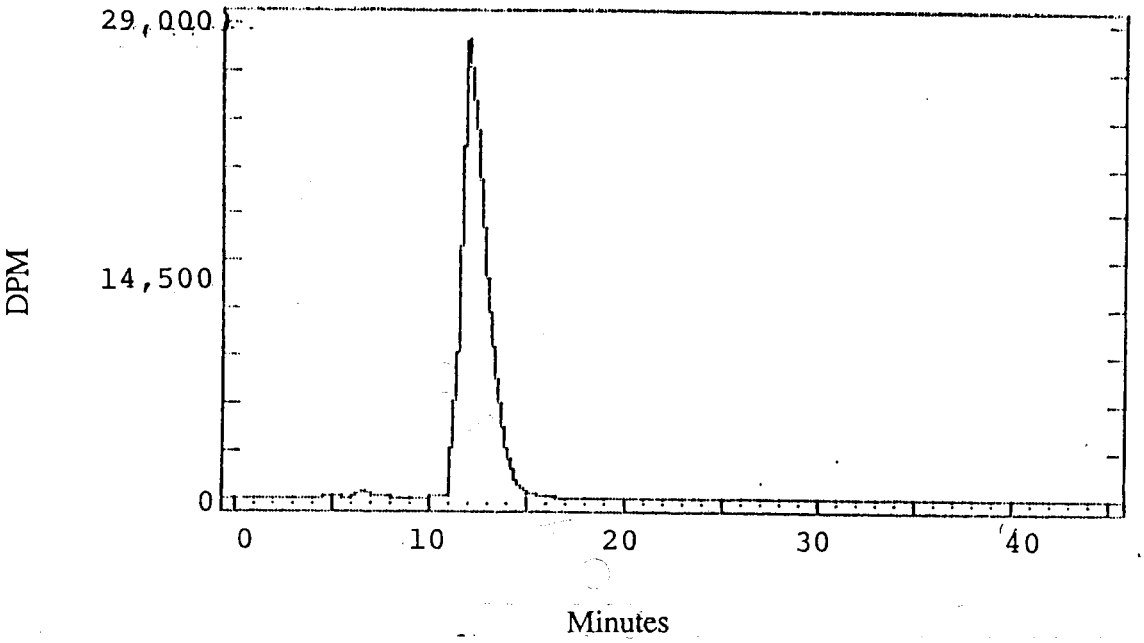

Figure 4. Radiochromatogram of Radiochemical Purity Analsyis of [^{14}C]DEF.

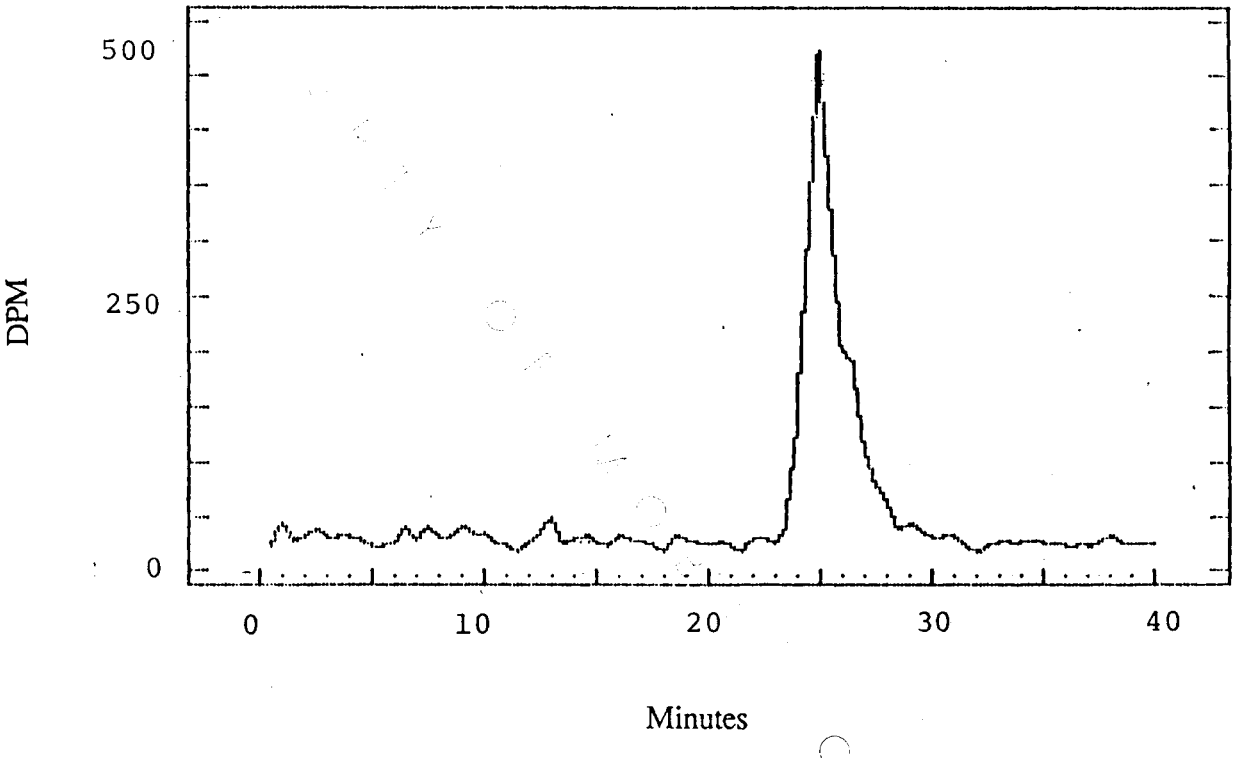

Figure 5. Representative Radiochromatogram From HPLC Analysis of [^{14}C]DEF. Day 30 Irradiated Replicate 1

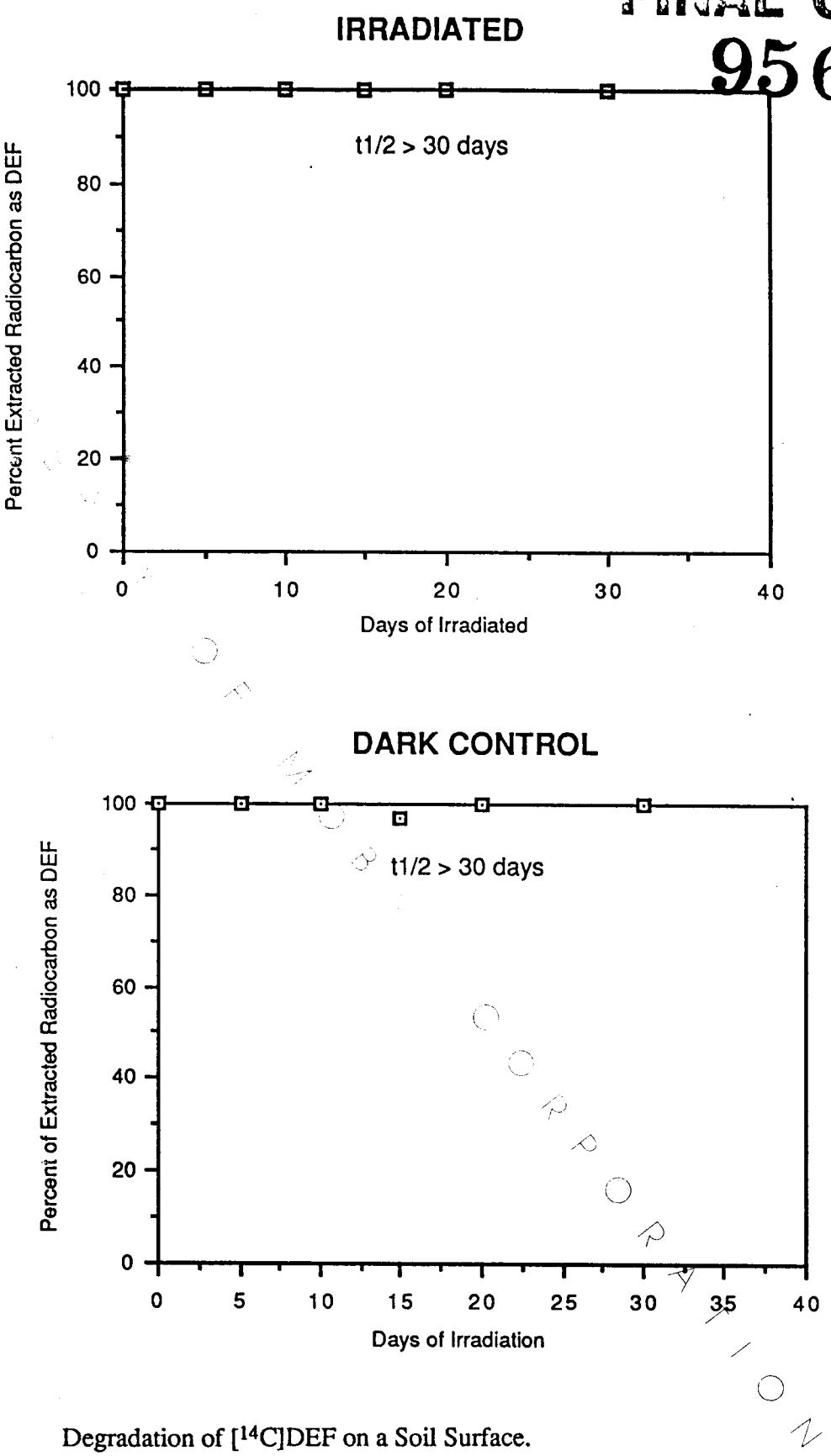

Figure 6. Degradation of [^{14}C]DEF on a Soil Surface.